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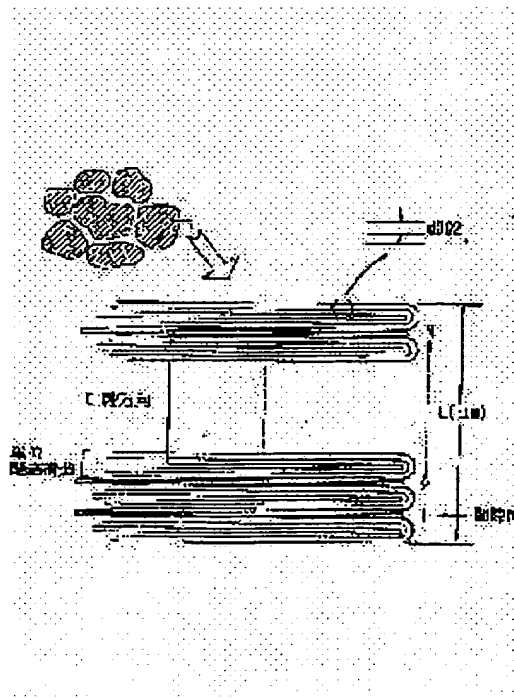
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(54) GRAPHITE MATERIAL SUITABLE FOR NEGATIVE ELECTRODE OF SECONDARY BATTERY OF LITHIUM ION AND ITS PRODUCING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To produce graphite powder suitable for negative electrode material of a secondary battery of lithium ion which has a high discharge capacity and a low capacity loss at a low cost.

SOLUTION: Carbon material containing B and Ti which is prepared by adding B raw material and Ti raw material before graphitization is subjected to the heat treatment for graphitization and, thereby, the graphite powder which includes B of 0.001-5.0 wt.% and Ti of 0.001-5.0 wt.% is obtained. Preferably, the carbon material is subjected to high speed crushing and/or shear crushing before graphitization or subjected to the heat treatment for oxidation and the heat treatment in inactive gas after graphitization. Thereby, the graphite powder, in which the spacing surface density of the closed structure formed by closing the end parts of c-plane



layers of the graphite on the powder surface by two layers increases to 100 pieces/ μm or more and which allows extremely high discharge capacity, is provided.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is the graphite which can produce the negative electrode of the rechargeable lithium-ion battery which it could manufacture by the approach of mass-producing from a cheap carbonaceous raw material, and discharge capacity was large, and was excellent in charge-and-discharge effectiveness since there were few capacity losses. (graphite) It is related with the rechargeable lithium-ion battery using powder, its manufacture approach, and this graphite powder, and its negative-electrode ingredient.

[0002]

[Description of the Prior Art] The rechargeable lithium-ion battery which is a nonaqueous electrolyte rechargeable battery which used the carbon material which functions a lithium ion reversibly as occlusion and an emitting host for the negative electrode, and used the organic solvent solution of lithium salt for the electrolytic solution has little self-discharge, use is quickly expanded focusing on the power source for pocket devices as a small rechargeable battery with high electromotive force and energy density, and use for large-scale applications, such as an electric vehicle and an object for stationary energy storage, is also expected in the future.

[0003] 372 mAh/g which is the geometric capacity of the LiC₆ presentation which is the intercalation compound by which the lithium ion was densely stored between the layers of a graphite in the negative electrode with which the geometric capacity of the negative electrode which consists of a metal lithium serves as about 3800 mAh/g from a carbon material compared with very high one It is thought that it becomes marginal capacity and capacity becomes much lower than a metal lithium. However, dendrite deposit at the time of the charge which is not avoided in a metal lithium negative electrode (this produces a short circuit and brings about aggravation of a cycle life, and increase of danger) Since it does not happen, the rechargeable lithium-ion battery which used the carbon material for the negative-electrode ingredient was developed, and it has spread quickly.

[0004] Graphitizing carbon which is the precursor of the graphite of a crystalline substance, and a graphite at the carbon material used for the negative electrode of a rechargeable lithium-ion battery (soft carbon) Nongraphitizing carbon which does not become a graphite even if it carries out elevated-temperature heat treatment (hard carbon) It is. Soft carbon and hard carbon are obtained by heat-treating the organic substance, such as a pitch and resin, until volatile matter is lost at about 1000 degrees C among an inert atmosphere. Crystallinity of hard carbon is low and it is a carbon material with amorphous structure. On the other hand, a graphite will be obtained if soft carbon is heat-treated at an elevated temperature about 2500 degrees C or more. Binder of usually impatience of the ingredient which carried out disintegration of any carbon material (generally organic resin) It is an electrode by making it stuck to the electrode substrate which uses, fabricates and serves as a charge collector by pressure. (negative electrode) It is manufactured.

[0005] Above-mentioned 372 mAh/g when a graphite is used for a negative electrode Although it becomes marginal capacity, since an actual discharge capacity becomes quite lower than this, bringing

close to this marginal capacity becomes a target from the surface activity site which checks invasion of a lithium ion, the death field to lithium ion storing, etc. existing.

[0006] Another trouble of the negative electrode of the rechargeable lithium-ion battery which consists of a graphite is charge-and-discharge effectiveness. Since surface reactivity of a graphite is high, a passive state coat tends to adhere with disassembly of the electrolytic solution at the time of charge. Since quantity of electricity used at this time serves as a loss, the difference of charge capacity and discharge capacity becomes large, and charge-and-discharge effectiveness falls.

[0007] There are many proposals until now about capacity increase of the carbon material negative electrode of a rechargeable lithium-ion battery. For example, using the carbide of the mesophase microsphere produced in the carbonization process of pitches is proposed by JP,4-115458,A, 5-234584, and 5-307958 each official report. If the regulation nature of the laminating array of a graphite layer is raised in the graphitized carbon fiber, high-capacity-izing is indicated by JP,7-282812,A.

[0008] The carbonization ingredient of the high capacity which uses special resin as a raw material is proposed by JP,6-187972,A, JP,3-245548,A -- boron 0.1 - 2.0 wt% -- organic resin to contain (an example, phenol resin) The carbonized carbonaceous ingredient is indicated. Since each of these uses an expensive raw material, raw material cost becomes high. moreover, nongraphitizing carbon with a low consistency (hard carbon) it is -- a sake -- per weight -- even if capacity is high, the capacity per volume becomes low. By the small cell it is decided that the volume will be, the capacity per volume is important.

[0009] It is a boron compound about the carbon powder obtained from the pitch in JP,8-31422,A. (an example, boron, boron carbide, boron oxide, boric acid) The carbon powder excellent in discharge capacity and charge-and-discharge effectiveness heat-treated and graphitized under existence is proposed. The aggregate which can be graphitized in JP,10-236808,A (an example, corks) Or a graphite and the binder which can be graphitized (an example, a pitch, organic resin) It is indicated that the graphite particle obtained by adding and graphitizing into mixture the graphitization catalyst chosen from iron, nickel, titanium, silicon, boron, these carbide, and a nitride is excellent in a rapid charge-and-discharge property with high capacity.

[0010]

[Problem(s) to be Solved by the Invention] It is indicated by JP,8-31422,A that the high graphitized-carbon powder of whenever [graphitization] which heat-treated and obtained carbon material under existence of boron serves as discharge capacity and a negative-electrode ingredient for rechargeable lithium-ion batteries excellent in charge-and-discharge effectiveness. Moreover, it is known from JP,10-236808,A etc. that boron is a graphitization catalyst.

[0011] When this invention persons examine the engine performance as a negative-electrode ingredient for rechargeable lithium-ion batteries of the graphitization powder graphitized and obtained under existence of boron, having just graphitized under existence of boron is not enough as improvement in discharge capacity, and a capacity loss increases conversely. (that is, charge-and-discharge effectiveness fall) It became clear that it carried out.

[0012] Discharge capacity of this invention is fully high, and its charge-and-discharge effectiveness is good, and it makes it a technical problem to offer the graphite powder which can be used as a negative-electrode ingredient for rechargeable lithium-ion batteries with few capacity losses, and its manufacture approach.

[0013]

[Means for Solving the Problem] By heat-treating and graphitizing the carbon material which added boron and titanium, as compared with the case of boron independent addition, discharge capacity improved, and charge-and-discharge effectiveness increased, and this invention persons found out that the small graphite powder of a capacity loss could be obtained.

[0014] By this invention, it is boron. 0.001 - 5.0 wt% and titanium Graphite characterized by containing 0.001 - 5.0 wt% (graphite) Powder is offered.

[0015] According to this invention, the manufacture approach of graphite powder characterized by including the process which heat-treats and graphitizes the carbon material containing boron and

titanium again is also offered.

[0016] If it is in a suitable mode, it has the lock out structure which the edge of the graphite c surface layer on the front face of powder connected the above-mentioned graphite powder of this invention two-layer [every], and was closed, and the gap surface density between these lock out structures in the direction of a graphite c-axis is 100. They are 1500 or less pieces/micrometer more than an individual / mum.

[0017] This connection edge is a laminating like [the structure which the two-layer ends which the graphite c surface layer approached connected, and was annularly closed here as it was typically indicated in drawing 1 as "the lock out structure which the edge of a graphite c surface layer connected two-layer / every /, and closed" is meant, and] illustration. (the example of illustration three layers) Structure may be taken.

[0018] A "gap side" means the field between the layers opened to the exterior between two adjoining lock out structures, as an arrow head shows to drawing 1. Like illustration, when each adjoining connection lock out structure is a laminated structure, ***** of the outermost layer of the laminated structure turns into a gap side. Lock out structure inserted between adjoining gap sides (irrespective of a multilayer or a monolayer) It considers as unit lock out structure.

[0019] It is defined as "the consistency of a gap side" as the number of the gap side per micrometer in the direction of a c-axis perpendicular to the c-th page of a graphite. The consistency of this gap side is substantially [as the consistency of unit lock out structure] the same.

[0020] The graphite powder which has the above-mentioned gap surface density was ground by one [at least] approach of high-speed grinding and shear grinding before ** carbonization and/or to the back. The approach characterized by including the process which heat-treats and graphitizes the carbon material containing boron and titanium, Or the process which heat-treats and graphitizes the carbon material containing the boron and titanium which were ground in front of ** carbonization and/or in the back, It can manufacture depending on whether it is the approach and ***** which are characterized by including the process which carries out surface treatment of the obtained graphite powder under the conditions which can delete the front face, and the process which heat-treats the graphite powder which carried out surface treatment at the temperature of 800 degrees C or more among inert gas.

[0021] According to this invention, the rechargeable lithium-ion battery equipped with the negative-electrode ingredient of a rechargeable lithium-ion battery which uses the above-mentioned graphite powder as a principal component, and the negative electrode created from this negative-electrode ingredient again is also offered.

[0022] As mentioned above, graphitizing under existence of the graphitization catalyst chosen from iron, nickel, titanium, silicon, boron, these carbide, and a nitride is indicated by JP,10-236808,A. However, using boron and titanium together as a catalyst is not indicated by this official report. Moreover, this catalyst changes the shape of particle of the obtained graphite powder, it is used in order to improve a rapid charge-and-discharge property, and the purpose differs from this invention.

[0023]

[Embodiment of the Invention] It is obtained by heat-treating and graphitizing the carbon material containing boron and titanium, and the graphite powder of this invention is boron. (B) 0.001 - 5.0 wt% and titanium (Ti) 0.001 - 5.0 wt% is contained.

[0024] If there are few boron contents of graphite powder than 0.001 wt%, during graphitization heat treatment, the function as a substantial graphitization catalyst will not be demonstrated, but progressing [of graphite structure] will become inadequate, and improvement in discharge capacity will not be accepted. On the other hand, if a boron content increases more than 5wt(s)%, the part which does not contribute to charge and discharge will increase, and an apparent capacity will fall. The range of a desirable boron content is 0.01 - 1.5 wt%.

[0025] If there are few titanium contents of graphite powder than 0.001 wt%, effectiveness by coaddition with boron cannot be acquired substantially, and increase of the capacity loss by about [that improvement in discharge capacity is not obtained] and boron addition cannot be controlled. If there are more titanium contents than 5wt(s)%, the part which does not contribute to charge and discharge will

increase, and an apparent capacity will fall. The range where a titanium content is desirable is 0.01 - 1.5 wt%.

[0026] If the addition stage of boron and titanium is before heat treatment for graphitization, it is good always. Generally graphite powder is manufactured through two steps of heat treatment processes, carbonization and graphitization, from a carbonaceous raw material. In this case, boron and titanium may be added to any of the carbonaceous raw material before carbonization, or the carbon material before graphitization. Mesophase which this raw material was heat-treated at low temperature from carbonization temperature, and the layer structure discovered it to some extent, and became an anisotropy optically when a carbonaceous raw material called especially tar and a pitch was used (a mesophase microsphere or bulk mesophase) If it carries out and this mesophase material is carbonized, it is known that layer-like graphite structure will tend to progress. In this case, boron and titanium may be added to the carbonaceous raw material before mesophase-izing, and any of the mesophase material after mesophase-izing. Of course, it is also possible to add during heat treatment of mesophase-izing or carbonization. It may add at a different stage or boron and titanium may be added to coincidence.

[0027] Boron and titanium can be added as the simple substance of these elements, or its compound. Although the ingredient which can be used is illustrated next, it is not restricted to these.

[0028] Boron raw material: Boron, boron carbide (B_4C etc.), boron oxide (B_2O_3 etc.), a boric acid (H_3BO_3 grade), and a metal boride (, such as TiB_2 , CrB , FeB , NiB , CoB , ZrB_2 , and AlB_2)
titanium raw material: -- titanium and titanium oxide (TiO , Ti_2O_3 , TiO_2 , and Ti_nO_{2n-1} sequence)
Titanium carbide (TiC), titanium nitride (TiN), titanium boride (TiB_2), a titanium chloride ($TiCl_2$, $TiCl_3$, $TiCl_4$), and titanium alloy (Ti-aluminum) etc. .

[0029] A desirable raw material is comparatively easy to receive, excluding any metals other than B and Ti. Specifically, it is TiB_2 which serves as both raw materials of TiO_2 , and boron/titanium in B_4C , B_2O_3 , and a titanium raw material from a boron raw material.

[0030] The addition of a boron raw material and a titanium raw material is the class of the raw material, an addition stage, and heat treatment conditions (temperature, an ambient atmosphere, time amount, etc.). Since evaporation differs, in consideration of manufacture conditions, it will experiment, if required and sets up suitably so that B and Ti of the specified quantity may be contained in the graphite ingredient which is an end product. However, even if especially titanium evaporates completely substantially during hot graphitization heat treatment, it can acquire discharge capacity increase of this invention, and the effectiveness of the fall of a capacity loss, so that it may mention later.

[0031] The graphite powder of this invention is c-axis (002) plane lattice spacing for which it asked by the lattice constant measuring method by the X diffraction. (d_{002}) 3.3650Å or less is 3.3600Å or less more preferably. C-axis (002) Plane lattice spacing (d_{002}) It is d_{002} to drawing 1 . It is displayed spacing between adjoining c surface layers, i.e., the distance between layers. Distance d_{002} between layers It is a crystalline index and is this d_{002} . A value becomes small and it is a value in an ideal graphite. ($=3.354^{**}$) The crystallinity of graphite powder is , so that it approaches. (the layer structure progressing) Discharge capacity increases. Depending on graphitization heat treatment conditions, the crystallinity of graphite powder has the inclination for crystalline high graphite powder to be obtained, so that time amount is so long that heat treatment temperature is high.

[0032] As mentioned above, the graphite powder of this invention can add boron and titanium before graphitization heat treatment, and can manufacture the carbon material containing boron and titanium as usual except for the point which carries out graphitization heat treatment.

[0033] Especially the carbonaceous ingredient used for carbonization is the same as that of what was not restricted but has been conventionally used for manufacture of a graphite, and is good. As an example of a carbonaceous raw material, they are the bulk mesophase which is the matrix of a coal-tar pitch or a petroleum pitch, the mesophase microsphere further produced by these heat treatments, and this microsphere and organic resin, or the organic substance. (an example, a polyacrylonitrile, rayon, or resin given in JP,2-282812,A) What was heated and carbonized is mentioned. Especially desirable carbonaceous raw materials are a mesophase microsphere and bulk mesophase.

[0034] A carbonaceous raw material is ground and carbonized and carbon material is obtained. Grinding

may be performed carbonization before at which [of Ushiro] time, and you may carry out by both Ushiro carbonization before. Grinding can be carried out using grinders of common use, such as a hammer mill, a fine mill, an attrition mill, and a ball mill. Desirable grinders are a hammer mill and some ball mills at the thing and representation target which perform impact crushing.

[0035] The carbonization conditions of the ground carbonaceous raw material are except the carbon which the raw material decomposed and was contained in the raw material. (except [when it is the raw material with which boron and/or titanium are already added] carbon, boron, and/or titanium) What is necessary is just to choose so that an element may be removed nearly completely. In order to prevent carbonaceous combustion, this carbonization heat treatment is carried out in an inert atmosphere or a vacuum. Carbonization heat treatment temperature is usual. It is within the limits of 800-1500 degrees C, and especially 1000-degree-C order is desirable. Although the heat treatment time amount which carbonization takes is based also on the class of raw material, heat treatment, and temperature, it is 30 minutes - about 3 hours in the case where temperature is 1000 degrees C.

[0036] The carbon material of the shape of powder acquired by grinding and carbonization is heat-treated and graphitized. When the boron and/or titanium of an initial complement are not added by carbonization, after adding boron and/or titanium to carbon material, graphitization heat treatment is performed. It graphitizes by existence of boron. (crystallization) Since the happening temperature falls, it can graphitize at temperature lower than the carbon material which does not contain boron. The range of heat treatment temperature of 1500-3000 degrees C is desirable, and it is 2000-3000 degrees C more preferably. Although the heat treatment temperature of 2500 degrees C or more is usually required when boron is not included, graphitization becomes possible from 2500 degrees C also at low temperature.

Moreover, when it graphitizes with the same heat treatment temperature, boron add-in material is more expensive than additive-free material for crystallinity. (d002 is small) Graphite powder can be obtained.

[0037] Some of boron added during two kinds of above-mentioned heat treatments, especially high graphitization heat treatment of temperature and titanium are removed from powder by evaporation or the pyrolysis in many cases. Especially titanium may be substantially removed from powder completely depending on graphitization heat treatment conditions. That is, although the obtained graphite powder is contained, it may not contain boron in the amount which can detect titanium. Thus, the graphite powder obtained although the reason was unknown even if titanium disappeared completely substantially during graphitization heat treatment is improvement in discharge capacity, and the fall (improvement in charge-and-discharge effectiveness) of a capacity loss. The effectiveness of this invention to say can fully be attained.

[0038] That is, in order to acquire the effectiveness of this invention, content of the titanium in the graphite powder obtained after heat treatment is not [that the carbon material before graphitization heat treatment should just contain titanium and boron in the manufacture approach of graphite powder] necessarily indispensable. In order to make homogeneity diffuse these more into carbon powder and for discharge capacity to obtain the fewer graphite powder of a capacity loss more highly in consideration of the amount of disappearance of the boron under heat treatment, or titanium, as for the boron to carbon material, and the addition of titanium, it is desirable to carry out to more than 0.01wt%, respectively.

[0039] For B of this invention, and Ti content graphite powder, the gap surface density between these lock out structures [in / it has the lock out structure which the edge of a graphite c surface layer connected two-layer / every /, and closed, and / the direction of a graphite c-axis] is 100. It is desirable that they are 1500 or less pieces/micrometer more than an individual / mum. Such graphite powder can show a very high discharge capacity.

[0040] The connection lock out structure and the gap side of graphite powder which were typically shown in drawing 1 can be observed with the high resolution electron microscope photograph of the cross section near the front face of graphite powder, and can ask for the consistency of a gap side from this electron microscope photograph. One example of such an electron microscope photograph is shown in drawing 2. Generally it consists of many fields where the directions of a c-axis differ, and graphite powder is each field. (namely, field of 1 lump with the same direction of a c-axis) It is called microcrystal. The graphite powder of this invention has the above-mentioned lock out structure, and the

value on the front face of powder of the gap surface density should just be the above-mentioned range. [0041] The direction which takes lock out structure has the edge of c surface layer chemically more stable than the structure where the edge has run out, and since the electrolytic solution cannot invade easily, a cycle property improves and charge-and-discharge effectiveness also becomes good. On the other hand, the gap side between the adjoining lock out structures serves as an invasion site of Li ion. The consistency in the direction of a c-axis of this gap side is 100. If fewer than an individual / mum, there are few invasion sites of Li ion and they cannot make discharge capacity very high. The upper limit of 1500 pieces/micrometer of gap surface density is the gap surface density at the time of taking the lock out structure of a monolayer between two-layer [which all c surface layers adjoin], i.e., the maximum gap surface density predicted theoretically.

[0042] The graphite powder which has above-mentioned lock out structure and gap surface density is the carbon material which received high-speed grinding or shear grinding before carbonization and/or in the back. (B and Ti content) It can manufacture by carrying out graphitization heat treatment. Hereafter, this approach is called 1st approach. The gap surface density of the graphite powder manufactured by the 1st approach is 100. Extent exceeding an individual / mum a little (an example and 100-120 an individual /mum) Usually it becomes.

[0043] The another manufacture approach (the 2nd approach) Heat treatment under the conditions which can delete the front face to B and Ti content graphite powder which were obtained by graphitization heat treatment if it depends (an example, oxidation heat treatment at the temperature of 600 - 800 **) It gives and heat-treats at the temperature more than 800 ** in inert gas further. The graphite powder in which this approach also has very high gap surface density can be manufactured.

[0044] Irregularity in the atomic level on the front face of powder introduced by grinding by the 1st approach (layer defect) The above-mentioned lock out structure is formed at the time of graphitization heat treatment. Therefore, grinding before graphitization processing is indispensable to obtain the graphite powder which has the lock out structure of high density. Since the introduced lock out structure may be destroyed by grinding when a layer defect will occur in c surface layer of the graphite generated by heat treatment, if grinding processing is carried out after graphitization heat treatment, it is not desirable to grind after graphitization heat treatment by the 1st approach. Therefore, it is desirable to grind so that it may become the last grain size before graphitization. However, slight grinding aiming at a crack may be carried out after graphitization.

[0045] The effect of the grinding conditions exerted on the crystal structure of graphite powder by the 1st approach is large. Gap surface density is 100. In order to obtain graphite powder with the lock out structure an individual / more than mum, in the case of the usual bang bang type grinder, it is necessary to adopt high-speed grinding. Moreover, it is the irregularity of atomic level equally on the front face of each powder. (layer defect) In order to make, the grinding time amount beyond fixed time amount is required. Concrete grinding conditions (an example, a rotational frequency, grinding time amount) Since it changes also with the classes of grinder and the classes of carbonaceous raw material to be used, gap surface density is 100 after graphitization heat treatment. What is necessary is for an experiment just to determine so that the graphite powder an individual / more than mum may generate and the powder of a desired grain size may be obtained. The 1st approach is followed and gap surface density is 100 after graphitization heat treatment by grinding other than shear grinding. The grinding conditions which the graphite powder an individual / more than mum generates are considered as high-speed grinding by this invention.

[0046] For example, in impact crushing, such as a hammer mill and an attrition mill, if it grinds beyond fixed time amount at the rotational frequency more than 5000 rpm, the graphite powder in which gap surface density has 100 or more lock out [/micrometer] structures after graphitization heat treatment can be obtained. When a rotational frequency is lower than this, even if it lengthens grinding time amount, the consistency of a gap side is 100. An individual / mum is not reached in many cases. Grinding time amount is adjusted according to a rotational frequency. The example of the desirable grinding conditions in a hammer mill is about 15 - 30 minutes in 5000 - 7500 rpm. However, this is instantiation to the last, and if the class of a grinder or raw material changes, a proper rotational frequency and grinding time

amount will also be changed.

[0047] Shear grinding which can introduce a layer defect efficiently since it becomes grinding mainly concerned with cleavage (grinding by the example and the disc mill) When adopting, it is not necessary to make grinding conditions high-speed. grinding by the disc mill -- for example, -- 150 - 300 rpm It can carry out about 2 to 10 minutes at the rotational frequency of extent. Shear grinding and other grinding may be used together. In that case, other grinding is good also as the above-mentioned high-speed grinding.

[0048] Especially grinding conditions are not asked by the 2nd approach. Moreover, you may grind after graphitization. It is oxidation heat treatment to the graphite powder obtained by graphitization heat treatment of the carbon material containing B and Ti by the 2nd approach. (or heat treatment for shaving off other front faces) Two heat treatments called heat treatment in an inert gas ambient atmosphere are performed.

[0049] Oxidation heat treatment performed first shaves off the front face of powdered c surface layer by oxidation, and it is performed in order to once open the lock out structure generated by graphitization heat treatment. By that cause, the lock out structure of c surface layer edge goes out on a powder front face, and c surface layer edges hardly connect, but the edge of c surface layer on the front face of powder serves as structure which gathered comparatively evenly.

[0050] The conditions of oxidation heat treatment are heat treatment temperature, although it will not be restricted especially if disconnection of lock out structure takes place substantially by oxidation. It is desirable to consider as 600 - 800 ** extent. It is because the graphite powder with lock out structure has high oxidation resistance, so it will be hard to oxidize if lower than 600 **, and oxidation progresses quickly above 800 degrees C and degradation of the whole graphite powder progresses. Although the time amount of oxidation heat treatment changes with temperature or throughput, generally it is 1 - 10 hours. A heat treatment ambient atmosphere is an oxygen content ambient atmosphere, and is a mixed-gas ambient atmosphere of oxygen and inert gas also in a pure oxygen ambient atmosphere. (an example, atmospheric air) .

[0051] As a result of a powder front face's being removed by this oxidation heat treatment, the weight of graphite powder decreases about 2 to 5%. Moreover, a powdered particle size becomes small slightly. (an example, about 1-2 micrometers) . If required, reduction of this particle size will be expected and grinding conditions will be set up.

[0052] In addition, disconnection of lock out structure is not restricted to oxidation heat treatment. Other approaches are also employable, if lock out structure can be opened wide and the laminated structure of flat c surface layer can be obtained by shaving off the surface structure of graphite powder. As other approaches, there is fluoride heat treatment or hydrogenation heat treatment, for example. What is necessary is just to set up the heat treatment conditions in this case suitably by experiment so that disconnection of lock out structure may take place.

[0053] Then, if graphite powder is heat-treated in an inert gas ambient atmosphere, the end of c surface layer opened wide will connect with the end of other c surface layers, and lock out structure will be again formed on the surface of graphite powder. Since flattening of the end of c surface layer on the front face of powder is carried out by oxidation heat treatment, the connection of c surface layer end at this time of two-layer [which was left] connecting is very rare. Consequently, the number of laminatings is small and serves as high lock out structure of gap surface density.

[0054] An inert gas ambient atmosphere is good at one sort, such as Ar, helium, and Ne, or two sorts or more. Heat treatment temperature should just be temperature which makes a comparatively big lattice vibration which can connect between c surface layer cause. If it heat-treats in an inert gas ambient atmosphere and sufficient lattice vibration is produced in order it is [energy] lower to have connected and to form lock out structure and to stabilize, the ends which c surface layer opened will connect. Generally the temperature more than 800 ** is required for this purpose. Especially an upper limit is not restricted. That lock out structure should just be formed, although heat treatment time amount changes with temperature, generally it is 1 - 10 hours. For example, at 1000 degrees C, about 5 hours becomes a standard.

[0055] Especially B and Ti content graphite powder concerning this invention are suitable as a negative-electrode ingredient of a rechargeable lithium-ion battery. As mentioned above, degree of crystallinity is high. (the graphite layer structure progressed) Since graphite powder can be obtained, discharge capacity serves as a high negative electrode. Moreover, since the increment in a capacity loss is controlled, charge-and-discharge effectiveness also becomes high. The gap surface density of lock out structure is 500 especially as mentioned above. More than an individual / mum, and very high graphite powder are 350 mAh/g near geometric capacity. A very high discharge capacity which is exceeded can be given.

[0056] When using the graphite powder of this invention for this application, creation of the negative electrode of the rechargeable lithium-ion battery using this can be performed by the same approach as usual. Generally, graphite powder is used as an electrode by casting on the charge collector used as an electrode substrate using a suitable binder. namely, negative-electrode ingredient (a negative electrode -- it is also called a mixture) Graphite powder is used as a principal component and it consists of what usually mixed the little binder to graphite powder. It is the foil of the metal of arbitration with which the elution by decomposition does not happen when the support nature of graphite powder is good and uses it as a negative electrode as a charge collector. (copper foil, such as an example, electrolytic copper foil, and rolling copper foil) It can be used.

[0057] Molding can be carried out by the suitable approach used in case an electrode is conventionally produced from a powder-like active material, fully pulls out the negative-electrode engine performance of graphite powder, and if ***** to powder is high and electrochemically [chemically and] stable, it will not be restricted at all.

[0058] For example, the binder and organic solvents, such as isopropyl alcohol, which become graphite powder from fluororesin powder, such as polytetrafluoroethylene and polyvinylidene fluoride, are added, kneaded and pasted. To graphite powder, How to screen-stencil this paste on a charge collector; Polyethylene, How to carry out thermocompression bonding to a charge collector at the same time it adds and blends resin powder, such as polyvinyl alcohol, dryly, and carries out the hotpress of this mixture and casts it using metal mold; Water-soluble binders, such as the above-mentioned fluororesin powder or a carboxymethyl cellulose, are further used as a binder for graphite powder. It slurs using solvents, such as N-methyl pyrrolidone, dimethylformamide or water, and alcohol, and this slurry is applied to a charge collector and the approach of drying etc. is mentioned.

[0059] The graphite powder of this invention can produce a rechargeable lithium-ion battery combining the nonaqueous electrolyte which dissolved the suitable positive active material and the suitable lithium compound which can be used for a rechargeable lithium-ion battery in the organic solvent.

[0060] as positive active material -- for example, lithium content transition-metals oxide [] -- $\text{LiM}_{12y}\text{M}_{2y}\text{O}_4$ (among a formula) $\text{LiM}_11\text{-xM}_2\text{xO}_2$ -- or -- X is $0 \leq X \leq 4$, Y is the numeric value of the range of $0 \leq Y \leq 1$, and M1 and M2 express transition metals. Consist of at least one kind of Co, nickel, Mn, Cr, Ti, V, Fe, Zn, aluminum, In, and Sn. a transition-metals chalcogen ghost and banazin san ghost (V_2O_5 and V_6O_{13} --) V_2O_4 and V_3O_8 grade $\text{MxMo}_6\text{S}_{8-y}$ And the lithium compound, a general formula (among a formula) X is $0 \leq X \leq 4$, Y is the numeric value of the range of $0 \leq Y \leq 1$, and M expresses metals including transition metals. Activated carbon, an activated carbon fiber, etc. can be used for the Chevrel phase compound and the pan with which it is expressed.

[0061] Although especially the organic solvent used for a nonaqueous electrolyte is not restricted For example, propylene carbonate, ethylene carbonate, dimethyl carbonate, Diethyl carbonate, 1, and 1- and 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactam, a tetrahydrofuran, 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, an anisole, Diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, One sort, such as chloro nitril, propionitrile, trimethyl borate, silicic-acid tetramethyl, nitromethane, dimethylformamide, N-methyl pyrrolidone, ethyl acetate, trimethyl alt.formate, and a nitrobenzene, or two sorts or more can be illustrated.

[0062] What is necessary is just to use organic [of fusibility], or an inorganic lithium compound for the organic solvent to be used as an electrolytic lithium compound. as the example of a suitable lithium compound -- LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 and $\text{LiB}(\text{C}_6\text{H}_5)$, LiCl , LiBr , LiCF_3SO_3 , and LiCH_3SO_3 etc. -- one sort or two sorts or more can be mentioned.

[0063]

[Example] (Example 1) About the bulk mesophase obtained from the coal-tar pitch, it is the hammer mill of an impact grinder. (Fuji Paudal u-mizer) It uses and is 10 kg at rotational frequency 7500 rpm. It ground for per 5 minutes. The obtained bulk mesophase powder was heated at 1000 degrees C under nitrogen-gas-atmosphere mind for 1 hour, it carbonized, and carbon material powder was obtained. To this carbon material powder, they are B and/or Ti raw material. (TiO₂, TiB₂, B-2 O₃) It added and mixed in the amount shown in Table 1, combining powder suitably. This mixed powder was put into the graphite crucible, it graphitized by carrying out a temperature up at the Atchison furnace to the predetermined temperature shown in Table 1 among atmospheric air, and graphite powder was obtained.

[0064] B of the obtained graphite powder and the analysis result of Ti content, and c-axis plane lattice spacing (d002) A measurement result is shown in Table 1 together with the discharge capacity of an electrode and the capacity loss which were produced from this graphite powder.

[0065] After B content of graphite powder added the calcium carbonate to the powder sample and ashed it by 800 in oxygen air current **, it added the sodium carbonate to these ashes, it was made it to heat and carry out melting by the burner, it dissolved melt in water, and measured it by carrying out quantitative analysis of the water solution by ICP emission spectrochemical analysis. Ti The content was measured like B content except having not added a calcium carbonate. C-axis plane lattice spacing (d002) The lattice constant measuring method by the least square method which includes the error of diffractometer from the X diffraction Fig. of a powder sample (an internal standard is not used) It computed. Indices of crystal plane (100) (101) (004) of an X diffraction Fig. (110) (112) (002) (006), All peak locations were used. Three X diffraction measurement is performed, the weighted average of the acquired value is taken, and it is d002. It considered as the value.

[0066] The obtained graphite powder was classified so that mean particle diameter might be set to about 15 micrometers, discharge capacity and a capacity loss mixed the :graphite powder 90 weight section and the polyvinylidene fluoride powder 10 weight section which produced the electrode as follows and were measured in the N-methyl-pyrrolidone of a solvent, made it dry and were made into the shape of a paste. After using a doctor blade and applying to homogeneity thickness on copper foil with a thickness of 20 micrometers it is thin to a charge collector in the obtained paste-like negative-electrode ingredient, it was made to dry at 80 degrees C. Area 1cm² started from here The test piece was used as the negative electrode.

[0067] Evaluation of a negative-electrode property was performed by the constant-current charge test by 3 pole type cel which used the metal lithium for the counter electrode and the reference pole. In the electrolytic solution, it is 1 mol/l in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and dimethyl carbonate. The solution in which LiClO₄ was dissolved by concentration was used.

[0068] Discharge capacity is an opposite Li reference pole (vs Li/Li⁺) at the current density of 0.3 mA/cm². It is the reference value for Li (vs Li/Li⁺) at the same current density after charging until potential is set to 0.0 V. Potential is +1.50V. It asked by discharging until it became. At moreover, this time (charge capacity) - (discharge capacity) It is a capacity loss (mAh/g) about a difference. It carried out.

[0069]

[Table 1]

試験No		黒鉛化 温度 (℃)	添加量 (wt%)			含有量 (wt%)		黒鉛の d002 (Å)	放電 容量	容量 ロス	実用 電池 容量 (mAh)
			TiO ₂	B ₂ O ₃	TiB ₂	B	Ti				
本 発 明 例	1	2900	0.1	4.0	—	0.50	0.001	3.3600	340	8	1643
	2	"	1.0	4.0	—	0.50	0.02	3.3560	350	8	1669
	3	2000	2.0	4.0	—	0.70	0.07	3.3650	331	8	1620
	4	2500	2.0	4.0	—	0.60	0.06	3.3600	340	8	1643
	5	2900	2.0	4.0	—	0.50	0.05	3.3560	350	8	1669
	6	"	3.0	4.0	—	0.50	0.10	3.3560	350	9	1666
	7	"	5.0	4.0	—	0.50	0.50	3.3560	348	9	1661
	8	"	8.0	4.0	—	0.50	1.50	3.3560	340	10	1638
	9	"	10.0	4.0	—	0.50	2.10	3.3560	335	11	1629
	10	"	20.0	4.0	—	0.50	5.00	3.3560	330	12	1619
	11	"	2.0	0.05	—	0.001	0.05	3.3645	335	7	1633
	12	"	2.0	0.40	—	0.02	0.05	3.3640	340	7	1646
	13	"	2.0	0.80	—	0.10	0.05	3.3600	345	7	1658
	14	"	2.0	5.0	—	1.50	0.05	3.3560	345	12	1646
	15	"	2.0	6.0	—	2.00	0.05	3.3560	336	13	1620
	16	"	2.0	10.0	—	5.00	0.05	3.3560	335	15	1621
	17	"	—	—	2.0	0.50	0.05	3.3570	345	11	1648
	18	"	2.0	—	2.0	0.50	0.10	3.3568	350	9	1666
比 較 例	19	"	—	—	—	ND	ND	3.3660	327	7	1613
	20	"	—	4.0	—	0.50	ND	3.3658	328	12	1603
	21	"	—	5.0	—	1.50	ND	3.3654	330	15	1600
	22	"	—	6.0	—	2.00	ND	3.3650	332	18	1597
	23	"	—	10.0	—	5.00	ND	3.3640	332	22	1587
	24	"	2.2	—	—	ND	0.05	3.3658	328	7	1617
	25	"	2.0	11.8	—	6.00	0.05	3.3560	330	16	1597
	26	"	22.0	4.0	—	0.50	6.00	3.3560	327	13	1597
本発明例	27	"	0.007	4.0	—	0.50	ND	3.3649	331	8	1620
	28	"	0.01	4.0	—	0.50	ND	3.3620	335	8	1630

[0070] As shown in Table 1, it is each about B and Ti. The graphite powder concerning this invention contained by 0.001 - 5.0 wt% of within the limits had a high discharge capacity, and was able to produce the negative electrode with few capacity losses. Moreover, d002 of the graphite crystal structure It was 3.3650Å or less and degree of crystallinity was high. Furthermore, even if graphitized at the temperature which is less than 2000 degrees C, graphite powder with a discharge capacity high enough was able to be obtained. Moreover, even if it changed Ti raw material and B raw material, such effectiveness was acquired similarly.

[0071] By carrying out concomitant use addition of Ti according to this invention compared with the example of a comparison which added only B, the function as a graphitization catalyst of B is reinforced and it is d002. Little graphite powder of a capacity loss was able to be obtained highly [discharge capacity] enough highly [it is small and / crystallinity] therefore. It turns out that a capacity loss will increase from Table 1 if B content becomes height, and there is an inclination for discharge capacity to fall if Ti content becomes height. Moreover, graphite powder with electrode engine performance sufficient at temperature lower than before of 2000-2500 degrees C was able to be obtained.

[0072] When the example of a comparison is seen, it compares with the example of this invention of the same graphitization temperature in the additive-free material which B and Ti both do not add, and is d002. It was large and discharge capacity fell. When only B was added and Ti was not added, even if it made [many] B content, discharge capacity did not increase, but the capacity loss increased conversely.

even if it added only Ti, although the improvement in discharge capacity was found, by adding B together, discharge capacity boiled it markedly and improved. When B content exceeded 5wt(s)%, the capacity loss became very large, and the capacity fall became remarkable when Ti content exceeded 5wt (s)%.

[0073] Trial No.27-28 show the case where titanium disappears completely substantially during graphitization heat treatment. These are within the limits about invention of the manufacture approach of the graphite powder of this invention, although it is out of range about invention of the graphite powder of this invention. (example of this invention) It is the becoming example. Even if titanium disappeared completely substantially and became undetectable during graphitization heat treatment so that the test result of these examples might show, discharge capacity was able to obtain graphite powder with few capacity losses highly.

[0074] (Example 2) The bulk mesophase obtained from the coal-tar pitch was used as a carbonaceous raw material, and graphite powder was prepared by three kinds of approaches as follows.

[0075] ** The same impact grinder as having used bulk mesophase in the example 1 (hammer mill) Or shear grinder (disc mill) Or both concomitant use (a hammer mill is used first) It ground on the conditions shown in Table 2. The obtained bulk mesophase powder was heated at 1000 degrees C under nitrogen-gas-atmosphere mind for 1 hour, it carbonized, and carbon material powder was obtained. To this carbon material powder, the powder of 2wt% TiO₂ and 4wt(s)% B-2 O₃ was mixed, and mixed powder was put into the graphite crucible, it heat-treated until it became 2900 degrees C among atmospheric air at the Atchison furnace, and the graphite powder containing B and Ti was obtained.

[0076] ** Graphite powder was obtained like upper ** to graphitization. After performing oxidation heat treatment of 3 hours for this graphite powder by 700 in oxygen ambient atmosphere **, 1000-degree C heat treatment was further performed in the argon ambient atmosphere for 5 hours.

[0077] ** Graphite powder was obtained like upper ** to graphitization. Oxidation heat treatment of 3 hours was performed for this graphite powder by 700 in oxygen ambient atmosphere **.

[0078] B of the obtained graphite powder and the analysis result of Ti content, and discharge capacity and a capacity loss (the above is measured like an example 1) It is shown in Table 2 together with the gap surface density of lock out structure. It asked for gap surface density by the observation which used the high resolution electron microscope photograph of a powder sample.

[0079]

[Table 2]

試験 No.	含有量 (wt%)		方 法	粉碎機の回転数/時間		間隙面 密度/ μm	放電 容量 (mAh/g)	容量 ロス	実用 電池 容量 (mAh)
	B	Ti		ハンマー ミル	ディスク ミル				
1	0.50	0.05	①	7500rpm/30分	—	105	349	12	1656
2	0.50	0.05	②	7500rpm/30分	—	770	355	12	1671
3	0.50	0.05	①	4500rpm/45分	—	79	335	12	1620
4	0.50	0.05	③	7500rpm/30分	—	閉塞構 造なし	356	25	1641
5	0.50	0.05	②	—	250rpm/5分	1199	354	12	1669
6	0.50	0.05	①	8000rpm/ 5分	200rpm/5分	1475	360	12	1684
7	0.50	0.05	①	—	250rpm/5分	103	348	12	1653

[0080] In approach **, it is a hammer mill as shown in Table 2. (impact grinder) When it grinds, gap surface density is 100 by high-speed grinding. The graphite powder an individual / more than mum was able to be obtained. Moreover, disc mill (shear grinder) Even if it uses it, gap surface density is 100. The graphite powder an individual / more than mum was able to be obtained. It is 350 mAh/g only at the discharge capacity of an electrode increasing and changing grinding conditions according to this gap surface density. A mass electrode which is exceeded was producible.

[0081] Approach ** also had large gap surface density, and was able to obtain graphite powder with a high discharge capacity. The graphite powder obtained on the other hand by approach ** which

performed only oxidation heat treatment after graphitization heat treatment did not have lock out structure, but the capacity loss became large.

[0082] (Example 3) In this example, the cylindrical rechargeable lithium-ion battery with the structure shown in drawing 3 was produced using the graphite powder obtained in the examples 1 and 2, and the cell engine performance was investigated.

[0083] The negative electrode 1 was produced from the negative-electrode ingredient which mixed the graphite powder 90 weight section and the polyvinylidene fluoride (PVDF) 10 weight section of a binder. After making both sides of band-like copper foil with a thickness of 10 micrometers it is thin to the negative-electrode charge collector 9 apply and dry the slurry of the shape of a paste prepared by making N-methyl pyrrolidone distribute this negative-electrode ingredient, compression molding was carried out and the band-like negative electrode 1 was produced.

[0084] A positive electrode 2 is a lithium carbonate 0.5. It produced from LiCoO_2 obtained by calcinating a mol and one mol [of cobalt carbonate] mixture by 900 °C among air for 5 hours. Obtained LiCoO_2 is JCPDS as a result of X diffraction measurement. Well in agreement with the peak of LiCoO_2 registered into the file. This LiCoO_2 was ground and classified, it considered as LiCoO_2 powder whose accumulation particle size is 15 micrometers 50%, 91 weight sections, the graphite 6 weight section of electric conduction material, and the PVDF3 weight section of binding material were mixed for the mixed powder which mixed this LiCoO_2 powder 95 weight section and the lithium-carbonate powder 5 weight section, and the positive-electrode ingredient was prepared. The paste-like slurry which made N-methyl pyrrolidone distribute this positive-electrode ingredient was pressed, after applying to homogeneity and drying both sides of band-like aluminium foil with a thickness of 20 micrometers it is thin to the positive-electrode charge collector 10, and the band-like positive electrode 2 was produced.

[0085] Subsequently, as shown in drawing 3, after carrying out the laminating of the separator 3 which consists of the band-like negative electrode 1, a band-like positive electrode 2, and a fine porosity polypropylene film with a thickness of 25 micrometers to the order of a negative electrode 1, a separator 3, a positive electrode 2, and a separator 3, it wound many times, and the eddy coil former electrode object with an outer diameter of 18mm was produced. This eddy coil former electrode object was contained with the iron cell can 5 which performed nickel plating. The electric insulating plate 4 was arranged in the upper and lower sides of an eddy coil former electrode object, and the positive-electrode lead 12 made from aluminum was drawn from the positive-electrode charge collector 10, and the negative-electrode lead 11 made from nickel was drawn on the cell lid 7 from the negative-electrode charge collector 9, and it welded to it at the cell can 5.

[0086] In the cell can 5 with which this swirl type electrode object was contained, it is LiPF_6 to the mixed solvent of the capacity factor 1:1 of ethylene carbonate and diethyl carbonate as an electrolyte. The solution of 1 M concentration in which it was made to dissolve was poured in. Subsequently, the cylindrical nonaqueous electrolyte rechargeable battery with a diameter [of 18mm] and a height of 65mm was produced by equipping the cell can 5 with the relief valve equipment 8 and the cell lid 7 which have a current cutoff device by the caulking through the insulating obturation gasket 6 which applied asphalt to the front face.

[0087] About each graphite powder, 50 cells were made as an experiment as mentioned above, and the engine performance of these cells was evaluated as follows. The result is written together in Tables 1 and 2. As shown in these tables, the rechargeable lithium-ion battery of high capacity is producible from the negative electrode containing the graphite powder of this invention.

[0088] The evaluation approach 1 of a cell Charge conditions: Maximum charge electrical-potential-difference 4.2 V and the amount one A2.5 of currents Time amount charge was performed.

[0089] 2) Discharge conditions : cell voltage discharged to 2.75V by the constant current of 700 mA.

[0090] 3) Cell capacity : discharge capacity was calculated by measuring a charging time value until cell voltage amounts to 2.75V in the constant current of 700 mA. For example, this time amount is 2.2. In being time amount, $700 \text{ mA} \times 2.2 \text{ h} = 1540 \text{ mAh}$ serves as discharge capacity. The maximum discharge capacity which repeated charge and discharge on the above-mentioned conditions, and was obtained in two to 5 early cycle was made into cell capacity. This example describes the average of 50 cells.

[0091]

[Effect of the Invention] According to this invention, while degree of crystallinity is high and excelling in discharge capacity by heat-treating the carbon material which made boron and titanium contain, and manufacturing graphite powder, there are few capacity losses and the graphite powder used as the negative-electrode ingredient of the rechargeable lithium-ion battery of high performance with high charge-and-discharge effectiveness is obtained. since graphitization can be carried out by heat treatment at the temperature of 1500-3000 degrees C -- an industrial use heat treating furnace -- enough -- it can carry out -- moreover, the carbonaceous ingredient of a raw material -- tar and pitch (this is used preferably, mesophase-izing it) etc. -- a cheap raw material can be used.

[Translation done.]